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INTRODUCTION

The tendency of a pollutant to accumulate in an organism depends upon the relative affinity of the chemical for the biological medium versus other environmental constituents. Bioaccumulation also depends upon the rates of chemical transport/transformation processes linking environmental sources of the pollutant to ultimate chemical sinks within the organism. A plausible hypothesis is that affinity relates directly to thermodynamic potential, with chemical transport/transformation in the direction of lower chemical potential. This prescribes that in the absence of contraints (kinetic, structural, or physiological) pollutants will move toward a state of equi-chemical potential of pollutant in a sink (such as organism tissue) relative to the source. Note that fugacity or absolute activity can be used in lieu of chemical potential and can be substituted throughout this paper without loss of meaning or generality. (See references of Mackay [1,2] for fugacity modeling.)

The pollutant concentrations in an aquatic organism at a

state of equi-chemical potential with the source defines maximal chemical uptake, from purely thermodynamic considerations. The ultimate model for biouptake incorporates thermodynamic driving forces into process kinetic modeling, but this requires highly specific characterization of the exposure environment, organism physiology and life habit, and pollutant reactivity (internal and external to the organism).

This document focuses on the role of sediment and sorption processes in bioavailability of environmental contaminants. A conceptual framework is presented for evaluating the thermodynamic potential for organic pollutant uptake by aquatic organisms, with special emphasis on sediment sources. Also, the role of desorption kinetics (or sorbed chemical accessibility) is discussed for cases where significant chemical depletion of the sediment in the exposure environment may result from chemical uptake by the organism.

CONCEPTUAL FRAMEWORK FOR ESTIMATION OF BIOCONCENTRATION POTENTIAL

The distribution of pollutant between sink and source at equi-chemical potential is independent of the actual pathway(s) of chemical exchange:

$$\frac{C^{e}_{sink}}{C^{e}_{source}} = D^{e}_{source,sink} \qquad (1)$$

where C denotes mass-referenced pollutant concentration; D denotes distribution coefficient, and e denotes the state of equi-chemical potential.

This path independence facilitates the estimation of a chemical distribution by not requiring pathway input, which is necessarily highly system specific. If one wishes to specify a pathway for computational purposes, however, the choice can be based on computational facility in lieu of real-world "realities," which are again highly system specific. The estimation of bioconcentration potential translates to the estimation of $D^{e}_{source,\ organism}$ for the particular organisms and/or sources in question.

Pollutant sources and sinks are commonly not homogeneous phases but may be comprised of highly composited mixtures of components with wide variability in their sorbing capability for the chemical(s) in question. For example, the major components of sediment particles can be grouped into minerals, organic materials, and amorphous oxides. Each is a prospective sorbent for aquatic pollutants but differs significantly in its (1) affinity for the pollutant (in a thermodynamic sense), (2) availability for sorption, and (3) nature of the sorption process (binding mechanism, site specificity, etc.).

In addressing chemical uptake, it is advantageous to subdivide such materials into independent distribution volumes, which are regions or components perceived to have fairly uniform potential for pollutant uptake (i.e., access, affinity, etc.). For a sediment particle, the aforementioned component breakdown provides a logical distribution volume factoring; for aquatic organisms, an appropriate factoring would likely discriminate tissue types (lipid, muscle, etc.). Chemical concentrations in a

pollutant source are expressed as weighted summations over all distribution volumes:

$$C_{source} = \sum_i X_i C_i \qquad (2)$$

where C_i are pollutant concentrations in individual distribution volumes, and X_i are the component mass fractions of each distribution volume active in sorption. Similarly, eqn 3 describes chemical concentrations in a sink:

$$C_{sink} = \sum_j X_j C_j \qquad (3)$$

The pollutant distribution coefficient between source and sink is given as:

$$D_{source,\ sink} = \frac{C_{sink}}{C_{source}} = \frac{\sum_j X_j C_j}{\sum_i X_i C_i} \qquad (4)$$

which can be expressed as a properly weighted summation of chemical distribution coefficients of sink/source components.

$$D_{source,\ sink} = \sum_j \frac{X_j}{\sum_i X_i C_i / C_j} = \sum_j \frac{X_j}{\sum_i X_i D_{ji}} \qquad (5)$$

Furthermore, at equi-chemical potential, the component distribution coefficients, D^e_{ji}, can be expressed as a ratio of pollutant activity coefficients in each phase:

$$D^e_{ji} = \frac{C^e_i}{C^e_j} = \frac{\gamma_j}{\gamma_i} \qquad (6)$$

These activity coefficients (denoted γ) quantify pollutant

affinity for a given phase.

Although it appears that eqn 1 through 6 have expanded a simple distribution coefficient ($D^e_{source,\ sink}$) into a cumbersome series of abstract quantities, this expansion facilitates a priori estimation of ($D^e_{source,\ sink}$) by factoring (to a large degree) source, sink, and chemical dependencies. The distribution-volume-factoring for a given type of source or sink depends on the type of pollutant in question (organic, inorganic, charged, uncharged, etc.); the weighting coefficients, X_i, X_j, however, are independent of chemical. Similarly, the preference factors contained in D^e_{ji} depend primarily on the chemical and component involved and are relatively independent of the component source. That is, an activity coefficient for pollutant in association with sediment organic carbon is largely independent of the sediment source. Likewise, an activity coefficient for a pollutant in animal lipid is independent of the individual animal. Therefore, source specificity exists largely in X_i, sink specificity in X_j, and chemical specificity in D^e_{ji}. Stated differently, source-to-source extrapolation derives from X_i, sink-to-sink from X_j; and chemical-to-chemical from D^e_{ji}.

What is frequently found in actual application is that this expanded framework shrinks considerably. Source and/or sink strength for pollutant release/uptake is usually localized in one or two distribution volumes. For example, in examining the potential for bioupteke of hydrophobic organics from sediment particles, one can assume the dominant distribution volumes to be the organic matter component of the sediment source and the lipid

component of the organism. In this case, eqn 4 is simplified as:

$$D_{\text{sediment, organism}} \approx \frac{X_l}{X_{oc}} \; D_{oc,l} \qquad (7)$$

where $D_{oc,l}$ is the distribution coefficient between animal lipid and sediment organic carbon. At a state of equi-chemical potential in the sediment and organism,

$$D^{e}_{oc,l} = \frac{\gamma_{oc}}{\gamma_l} \qquad (8)$$

The biological uptake of hydrophobic organic pollutants from sediment sources should depend, to a first approximation, on the organic carbon content of the sediment, the lipid content of the organism, and the relative affinities of the chemical for sediment organic carbon versus animal lipid.

Furthermore, for these pollutants, one would not expect large variations in either γ_{oc} or γ_l (at most 10 fold) from chemical-to-chemical. Besides, chemical-to-chemical variation in γ_{oc} should be highly correlated with changes in γ_l, and therefore, $D^{e}_{oc,l}$ should be highly chemical independent. Thus, one can postulate, the thermodynamic potential for hydrophobic organic pollutant uptake by an aquatic organism from a sediment source should be highly independent of chemical, depending only on the organic carbon content of the source and the lipid content of the organism (Figure 1):

$$D^{e}_{\text{sediment, organism}} \approx \frac{X_l}{X_{oc}} \; D^{e}_{oc,l} \qquad (9)$$

The numerical value of the chemical preference factor between animal lipid and sediment organic carbon must be determined experimentally but should be on the order of unity. Initial tests of this approach [3] suggest this preference factor to be approximately 2.

This postulated behavior is strikingly simplistic and needs further testing. Obvious refinements are possible, but one should be aware that the power of the postulate derives from its simplicity. Possible refinements include (1) bringing in additional distribution volumes in either the sediment or organisms or (2) fine tuning the preference factors (D^{e}_{ji}) for the specific chemical, sediment, and organisms involved. Ultimately, chemical transport and physiological process kinetics can be introduced that are necessarily highly system specific (not to mention complex).

For purposes of environmental decision-making, points of advocacy for a thermodynamic approach for estimating biouptake potential include two considerations:

- o The approach can be implemented. Predictive equations can be easily formulated, calibrated, and tested.
- o A conceptual framework can be developed that can be easily adapted to describe standard exposure test conditions, or extended to include kinetic considerations.

SORPTION KINETICS: RELATIONSHIP TO BIOAVAILABILITY

In cases where significant depletion of the sorbed pollutants on the sediment results from chemical uptake by an organism,

accessibility of sorbed chemicals can limit biouptake. In most exposure environments involving sediment, this will probably not occur at the bulk system level (i.e., organisms typically constitute a minor sink for pollutants relative to sediments). Such may not be the case, however, at the microenvironment level (i.e., within organism burrows or in regions contiguous to organism membranes active in chemical uptake). In such cases, desorption kinetics may affect rates of chemical uptake by aquatic organisms. With short exposure (minutes to a few hours), a major portion of the total sorbed chemical may be inaccessible for biouptake, regardless of local thermodynamic gradients driving the overall process. There are no data presently available that directly address sorbed chemical accessibility for biouptake.

The sorption literature reveals a great deal of confusion regarding the rate (or extent) of chemical desorption with process descriptions ranging from "easily reversible" to "irreversible."

Recent studies [4-7 and DiToro, Personal communication] suggest that uncharged sorbates are not irreversibly bound to sediments, but in cases where chemicals have incubated for extended periods in sediment, a significant portion of the total sorbed chemical is highly resistant to release. This nonlabile character appears to derive from physical inaccessibility; the sorbed chemical is buried within the sediment particle, perhaps in an aggregate structure or within a sorbent component such as organic matter. The term aggregate in this context includes any

of a wide variety of naturally occurring particle assemblages, from loosely agglomerated sediment particles or clay mineral tactoids to more highly structured micelles or layered lattice clay minerals (see Lick [8] for discussion of aggregation). Chemical release appears to be primarily mediated by intraparticle diffusion, although release may involve aggregate fracture. Fixed-geometry diffusion models [9] and a two-box linear model [4,5] have been used to describe sorption kinetics. Fixed-geometry models more accurately describe the temporal sorption behavior where applicable, but they are highly restrictive in scope (i.e., range of system variables, such as time, solids concentration, etc. over which a given model is applicable).

Sediment particle size and structural variability (inherent in a given sediment or between sediments) seems to preclude the general applicability of any single fixed-geometry model. The two-box model is much more general, with no definition of particle geometry or sorbate release mechanism. The model simply discriminates a labile or rapid equilibrium sorption component (requiring at most a few hours to achieve) and a nonlabile or resistant component that may require days, weeks, or even months to achieve. Over a broad range of sediments and hydrophobic sorbates, the labile component accounted for from 1 to 60% of the total sorption. In general, the labile fraction varied inversely with the solids concentration and equilibrium sorption constant [4,5].

At very low solids concentrations (50 mg/L or less), roughly

half the total sorption was labile for all sorbates tested, but this component decreased with increased solids, becoming vanishingly small for highly sorbed chemicals. The rate constant for accessing the nonlabile component varied inversely with the equilibrium constant. For equilibrium constants of 10^2, 10^3, 10^4, 10^5, the corresponding times-to-equilibrium were roughly a day, week, month, year, respectively [5].

The potential relevance of release kinetics to biouptake kinetics is obvious. In regions contiguous to uptake membranes, the aqueous phase may be depleted of chemical, thus inducing desorption from sediment particles within the region. The maximal release that can be effected, however, is the labile component. In spite of this kinetic limitation, sediments can still enhance uptake rates substantially (relative to water alone) in many circumstances by increasing the total pollutant flux to uptake membranes.

A similar kinetic role of sediments applies to chemical excretion if the thermodynamic gradients are reversed. For example, the presence of uncontaminated sediments in a region contiguous to an excretion membrane can enhance excretion rates, but the full sorption potential is not realizable during brief contact periods. At equilibrium, the same thermodynamic equations developed previously for uptake apply.

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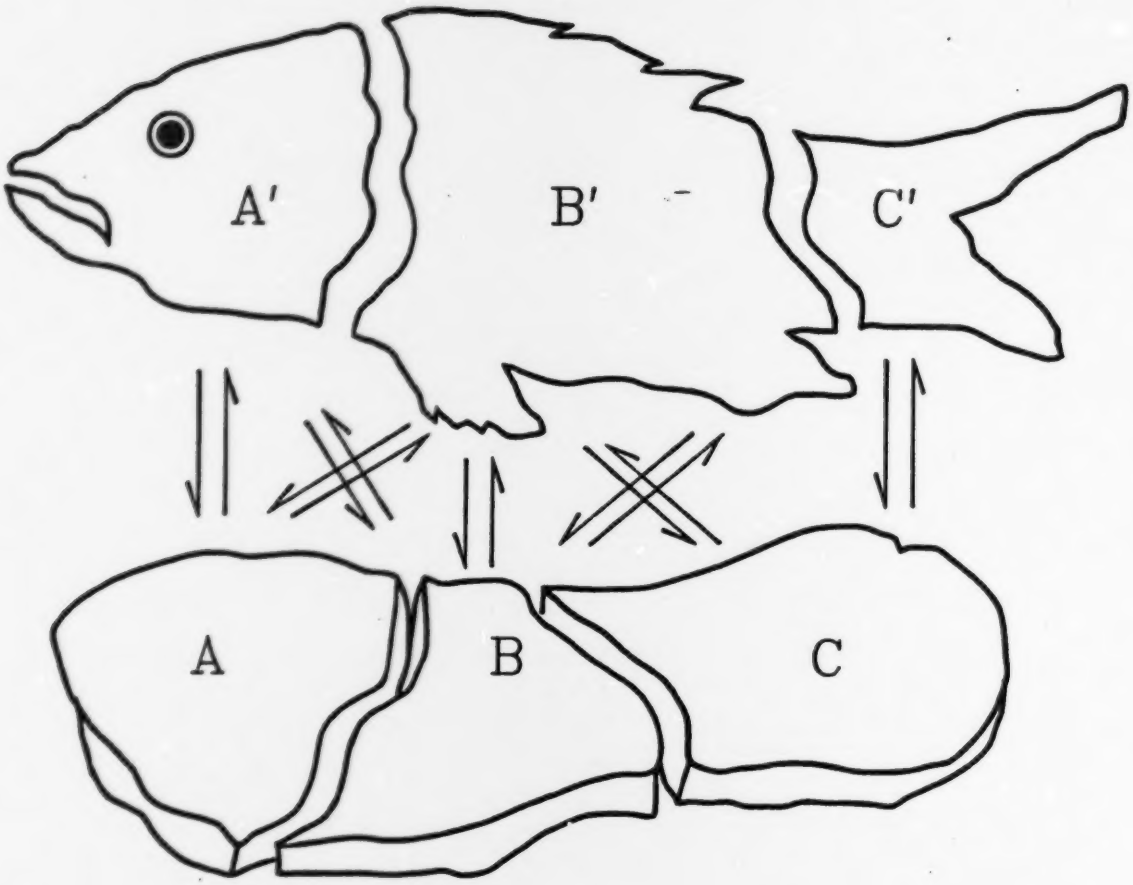

$$\frac{C^{e}_{organism}}{C^{e}_{sediment}} = \sum_{j} \frac{X_j}{\sum_{i} X_i D^{e}_{ji}}$$

$$\approx \frac{X_l}{X_{oc}} D^{e}_{oc,l}$$

Figure 1. Distribution of pollutant between sediments and aquatic organisms at a state of equi-chemical potential.